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Simple Circular Dichroic Method for the Determination of Absolute Configuration of 5-Substituted 2(5*H*)-Furanones

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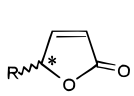
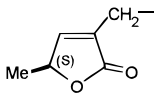
Chiral 2(5*H*)-furanones (butenolides) have emerged as important synthetic intermediates for which several general synthetic protocols have been devised.[1,2] In these compounds (A), the stereogenic center is most frequently located at C(5).



(A)



(B)

Hanessian[3] extensively used (*S*)-5-(hydroxymethyl)-2(5*H*)-furanone (A, R = CH_2OH) derived from (*S*)-glutamic acid in the synthesis of polypropionates and polyols and applied it in cycloadditions and conjugate addition reactions. Alternative routes to optially active butenolides involve D-ribonolactone, D-mannitol, or levoglucosenone as starting materials.[4] Optically active 5-alkyl-substituted butenolides have been explored by several groups.[5] A chromium carbene route to optically active 5-alkoxy-5-alkyl-2(5*H*)-furanones was recently described by Hegedus and co-workers.[6]

The chemistry of γ-alkoxybutenolides has been explored in our laboratory.[7] Diastereomerically pure butenolides have been prepared with the aid of a chiral auxiliary, (+)- or (−)-menthol (A, R = menthyloxy).[2] Racemic 5-alkoxy-2(5*H*)-furanones were kinetically resolved by the addition of thiols catalyzed by cinchona alkaloids.[8] Efficient resolution of γ-alkoxybutenolides through inclusion complexation with chiral host compounds derived from tartaric acid has been reported,[9] while 5-(acyloxy)-2(5*H*)-furanones were resolved via lipase-catalyzed transesterification reactions.[10]

Optically active butenolides can also be prepared by diastereoselective addition of a chiral tin(II) enolate to γ-hydroxybutenolides,[11] and γ-C-glycosylated butenolides are available from aldehydosugars through condensation with 2-(trimethylsiloxy)furan.[12] The 2-(trimethylsiloxy)-furan−butenolide pathway was employed in the synthesis of 6-deoxy-6,6,6-trifluorosugars.[13] Optically active butenolides are furthermore available from sugar lactones[14] and from chiral propargylic alcohols via ruthenium-catalyzed Alder ene reactions.[15]

γ-Alkyl- and γ-alkoxybutenolide structures are frequently found in several biologically active compounds, e.g., strigol[16] and marine natural products.[17,18] In addition, chiral 5-methyl-substituted 2(5*H*)-furanone rings are structural components of numerous natural products, examples of which are acetogenins,[19] muconolactones,[20] and leptosphaerin.[21] Compounds of these classes are frequently unsuitable for X-ray crystallographic studies due to their waxy nature; hence, in such instances the absolute configuration of the butenolide fragment may not be known.

The need for a rapid and universal method for the determination of the absolute configuration of synthetic butenolides is obvious because of their frequent use as intermediates in asymmetric synthesis.[22] So far, chemical correlations have been necessary to determine the absolute configuration.[23]

Despite the importance of chiral butenolides in synthesis and in natural products chemistry the chiroptical data for these compounds are scarce[24] and their relation to the structure has been discussed mainly in the case

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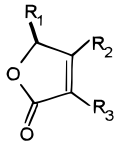
Chart 1



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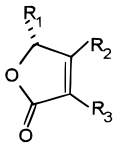


10 - 18

1 $R_1 = (CH_2)_2OH$, $R_2 = R_3 = H$

2 $R_1 = CH_2COOH$, $R_2 = R_3 = H$

3 $R_1 = CH_2COOMe$, $R_2 = R_3 = H$

4 $R_1 = (R)$-$CH(OH)CF_3$, $R_2 = R_3 = H$

5 $R_1 = (S)$-$CH(OSiMe_2tBu)CF_3$, $R_2 = R_3 = H$

6 $R_1 = OMe$, $R_2 = R_3 = H$

7 R_1 = O-(-)-menthyl, $R_2 = R_3 = H$

8 R_1 = O-(-)-menthyl, $R_2 = Me$, $R_3 = H$

9 R_1 = O-(-)-menthyl, $R_2 = H$, $R_3 = Me$

10 $R_1 = CH_2OH$, $R_2 = R_3 = H$

11 $R_1 = CH_2OSiMe_2tBu$, $R_2 = R_3 = H$

12 $R_1 = CH_2OC(O)tBu$, $R_2 = Me$, $R_3 = H$

13 $R_1 = (R)$-$CHCH_2OCMe_2N(Boc)$, $R_2 = R_3 = H$

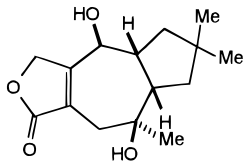
14 $R_1 = (R)$-$CH(OH)CF_3$, $R_2 = R_3 = H$

15 R_1 = OAc, $R_2 = R_3 = H$

16 R_1 = OiPr, $R_2 = R_3 = H$

17 R_1 = O-(+)-menthyl, $R_2 = R_3 = H$

18 R_1 = O-(+)-menthyl, $R_2 = H$, $R_3 = Me$



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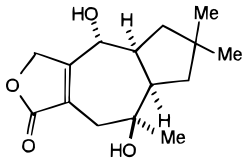


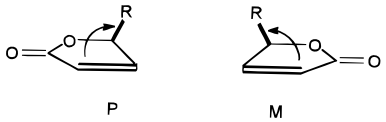
20

of bi- and polycyclic 2(5*H*)-furanones.[25] Beecham discussed the effect of ring nonplanarity in polycyclic butenolides on the n−π* transition rotatory strength,[25a] and Richardson examined this effect by the INDO-MO calculations.[25b] Uchida and Kuriyama studied the $\pi-\pi$* Cotton effect of mono- and polycyclic α,β-unsaturated γ-lactones and found that the sign of the Cotton effect correlates with the configuration of the more polarizable bond at γ carbon atom.[25c] Our analysis of the CD data of 5-substituted 2(5*H*)-furanones takes advantage of the well-established planarity of the butenolide ring.[2,26] The α,β-unsaturated lactone chromophore in the butenolide ring is achiral, and it becomes optically active in the presence of a perturber at the stereogenic center at C(5). The observed Cotton effects due to the n−π* and $\pi-\pi$* transitions of the α,β-unsaturated lactone chromophore may be correlated directly to the absolute configuration of the stereogenic center. This approach has been successfully applied to planar 2-cyclopentenones bearing an oxygen substituent at C(4).[27]

Here we report the results of our CD studies of a series of 5-alkyl- and 5-alkoxy-substituted butenolides **1**−**18** (Chart 1).

The 5-(menthyloxy)- (**7**−**9**, **17**, and **18**),[2] 5-methoxy- (**6**), and 5-isopropoxybutenolides (**16**)[9] were prepared as previously described. Optically active 5-acetoxy-2(5*H*)-furanone (**15**)[10] was obtained in 31% yield via enzymatic kinetic resolution of racemic **15**. When lipase PS immobilized on Hyflo Super Cell in *n*-hexane:*n*-butanol (3:1) was used, a transesterification occurred and the starting material recovered after 4 h was enantiomerically pure (ee > 99% as determined by chiral GC). The absolute configurations of all the butenolides except for **15** and **16** are known from chemical correlation and the absolute configuration of 5-(hydroxymethyl)-2(5*H*)-furanone and *d*- or *l*-menthol. The CD data of all butenolides are given in Table 1.

From the data of Table 1 it can be readily seen that absolute configuration at C(5) is correlated to the sign of the Cotton effects of the n−π* (235−250 nm) and $\pi-\pi$* (200−220 nm) transitions according to Figure 1. Thus, right-handed (P) helicity of the R−C(5)−C═C bond



P M

n-π* (235 - 250 nm)	$\Delta\varepsilon < 0$	$\Delta\varepsilon > 0$
$\pi-\pi$* (200 - 215 nm)	$\Delta\varepsilon > 0$	$\Delta\varepsilon < 0$

Figure 1. Correlation of the butenolide Cotton effects with absolute configuration.

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Table 1. CD and UV Data for Chiral 2(5*H*)-Furanones

compd	CD, $\Delta\epsilon$ (nm)		UV, ϵ (nm)
	n−π*	π−π*	π−π*
1	−0.1 (239)	+6.7 (203)	6300 (207)
2	−0.2 (239)	+5.5 (202)	6800 (205)
3	−0.3 (239)	+7.0 (201)	8700 (205)
4	−0.3 (242)	+6.4 (205)	7200 (204)
5	−0.4 (242)	+10.9 (206)[a]	7900 (204)
6	−2.3 (249)	+1.9 (203)	6500 (201)
7	−1.9 (248)	+5.6 (201)	6300 (201)
8	−3.7 (242)	+7.5 (214)	9500 (207)
9	−2.4 (245)	+4.7 (212)	7400 (203)
10		−13.0 (209)	7200 (206)
11		−13.5 (207)	7100 (206)
12	+0.6 (236)	−10.0 (207)	11 600 (208)
13		−5.8 (220)	5300 sh (220)
14	+0.2 (243)	−8.0 (205)	7600 (204)
15	+2.3 (250)	−13.6 (198)	6900 (201)
16	+0.75 (248)	−2.6 (201)	6400 (201)
17	+1.9 (249)	−5.7 (201)	6300 (201)
18	+2.7 (247)	−6.0 (213)[b]	
19	+1.8 (241)	−3.4 (218)	
20	−0.3 (250)	+6.0 (222)	

[a] De 88%. [b] Data from ref 24. Solvent: acetonitrile.

system (where R is an alkyl or alkoxy group) gives rise to a negative n−π* and a positive π−π* Cotton effect. Opposite sign pattern is observed for left-handed (M) helicity of the bond system mentioned above.[28]

The following characteristic features are observed: (i) the rule works regardless of an additional chiral center in the substituent R (compounds **4**, **5**, **7**−**9**, **13**, **14**, **17**, **18**); (ii) the rule can also be applied to butenolides bearing additional methyl groups attached to the C=C bond (compounds **8**, **9**, **12**, and **18**); (iii) Cotton effects associated with the n−π* transition are weak except for 5-alkoxy-substituted 2(5*H*)-furanones. For example, the n−π* Cotton effect is not observed for **10**, **11** and **13** (in methanolic solution). Therefore it is generally advisable to correlate the absolute configuration with the sign of the π−π* Cotton effect.

As a corollary it seems that the sign of rotation of the butenolide[22] at the sodium D-line can be related to its absolute configuration. In the absence of a chiral center other than at C(5) the rotation is determined primarily by the sign of the strong Cotton effect of the π−π* transition; i.e., it is positive for P-helicity and negative for M-helicity of the R−C−C=C bond system (Figure 1). The relation between the absolute configuration and the rotation has been previously observed on a purely experimental basis for γ-C-glycosylated butenolides,[12a] and it holds for many other butenolides having chiral substituents at C(5) such as the menthyloxy group (**7**−**9**, **17**, and **18**); see, however, ref 11. It needs to be emphasized that such a relationship should be treated with care, and analysis of the CD spectra provides a far more reliable way of determining the absolute configuration of butenolides.

On the basis of the rules presented here, the 5(*S*) configuration could now be assigned to (−)-5-acetoxy-2(5*H*)-furanone (**15**) and (−)-5-isopropoxy-2(5*H*)-furanone (**16**) from their CD spectra.

The configurational rule can be particularly useful for determining the absolute configuration of the butenolide moiety in acetogenins, previously possible only through synthesis.[29] Thus, acetogenins bearing the 5-methyl-2(5*H*)-furanone group of (*S*)-configuration (B) as the sole chromophore display a negative n−π* Cotton effect at 235−240 nm and a positive π−π* Cotton effect at 205−210 nm.[30,31]

The configurational rule also seems to be applicable to 2(5*H*)-furanones having an allylic hydroxy group in a ring fused to the butenolide ring. The two diastereoisomeric lactarorufins[32] LRA (**19**) and *epi*-LRA (**20**) display Cotton effects of opposite signs, and in each case the signs of the n−π* and π−π* transition Cotton effects follow the helicity rule for the HO−C−C=C bond system.

Experimental Section

UV and CD spectra were recorded with a Shimadzu 160 spectrophotometer and a Jobin-Yvon III dichrograph, respectively, in methanol solutions (10^{-3} M).

Butenolides **6**, **16**,[9] **7**−**9**, **17**, and **18**[2c] were prepared following reported procedures.

(*R*,*S*)-5-Acetoxy-2(5*H*)-furanone ((*R*,*S*)-15). To a mixture of 5-hydroxy-2(5*H*)-furanone (22.8 g, 227 mmol) and acetic anhydride (24.75 g, 242 mmol) was added a catalytic amount of *p*-toluenesulfonic acid. The solution was heated to 50 °C for 2.5 h, and the product was distilled to provide 28.99 g (89%) of (*R*,*S*)-**15** as a pale yellow oil: bp 102−104 °C (0.05 mmHg); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.32 (dd, 1H, J = 5.6, 1.3 Hz), 6.95 (d, 1H, J = 1.2 Hz), 6.30 (dd, 1H, J = 5.6, 1.3 Hz), 2.13 (s, 3H); ^{13}C NMR (50 MHz) δ 168.90, 169.50, 149.80, 125.09, 93.76, 20.56.

Transesterification of (*R*,*S*)-5-Acetoxy-2(5*H*)-furanone. To a solution of racemic **15** (8.00 g, 56.3 mmol) in 1.5 L of a mixture of *n*-hexane:*n*-butanol (3:1) was added 3.0 g (30 m/m %) of lipase PS immobilized on Hyflo Super Cell. The mixture was vigorously stirred at room temperature, and the progress of the reaction and the enantiomeric excess were monitored by chiral GC (capillary column coated with CP cyclodextrin-b-2,3,6-M-19). After 4 h, an ee > 99% was found and the stirring was stopped. After precipitation of the solid material (10 min) the solution was decanted from the enzyme slurry and filtered through Celite. The solvents were removed by distillation under vacuum at room temperature, and the remaining yellow oil was purified by chromatography (silica gel, hexane:EtOAc 3:1). Pure **15** was obtained as an oil (2.55 g, 31.8%): $[\alpha]_D$ = +25.4 (*c* 1.00, $CHCl_3$).

Acknowledgment. We gratefully acknowledge the following groups that provided us with the samples for CD study: Prof. A. Sutherland (**1**−**3**),[20b] Prof. T. Yamazaki (**4**, **5**, **14**),[13] Prof. J. Font (**12**),[33] Prof. P. Garner (**13**),[34] and Prof. Daniewski (**19**, **20**).[32] J.K.G. thanks the Committee for Scientific Research (KBN) for partial support. This work was sponsored in part (A.v.O., H.v/d D., B.L.F.) by the Netherlands Foundation for Scientific Research (NWO/SON) and (C.W.L.) by the EC project Stereoselective Organic Synthesis (Human Capital and Mobility Network).

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(28) It is apparent that of the two allylic bonds at C(5), C-alkyl (or C-alkoxy), and CH, each having opposite helicity relation to the C=C bond, the former, more polarizable, has a dominating effect on the sign of the π−π* Cotton effect; see earlier work on allylic axial chirality effect: (a) Beecham, A. F.; Mathieson, A. McL.; Johns, S. R.; Lamberton, J. A.; Sioumis, A. A.; Batterham, T. J.; Young, I. G. *Tetrahedron* **1971**, *27*, 3725. (b) Beecham, A. F. *Ibid.* **1971**, *27*, 5207. (c) Scott, A. I.; Wrixon, A. D. *Ibid.* **1971**, *27*, 4787. (d) Totty, R. N.; Hudec, J. *J. Chem. Soc., Chem. Commun.* **1971**, 785. (e) Burgstahler, A. W.; Barkhurst, R. C.; Gawronski, J. K. In *Modern Methods of Steroid Analysis*; Heftmann, E., Ed.; Academic Press: New York, 1973; pp 349−379.

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